

POLYSACCHARIDE SURFACTANTS: PREPARATION, SYNTHESIS, CHARAKTERIZATION AND PROPERTIES

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ABSTRACT: This contribution deals with partial hydrophobization of O-(carboxymethyl)starch (CMS, DS = 0.3) with alkylamine (C₆, C₁₀, C₁₂). The reaction was performed in methanol or dimethylsulfoxide (MeOH, DMSO) and 4-DMAP as catalyst at laboratory temperature and compared to the reaction performed by the assistance of microwave energy.

Various reaction conditions were studied in order to optimize the preparation of water-soluble CMS alkylamides. The obtained derivatives were characterized by FT-IR spectroscopy and the surface-active properties were determined by surface tension and emulsifying efficiency. The biosurfactant performance of the prepared alkylamides of CMS were tested by washing power and antiredeposition efficiency.

KEY WORDS: CMS, amidation, hydrophobization, surface active - properties

1. INTRODUCTION

In recent years, considerable attention has been devoted to the preparation of biosurfactants from commercial and non-commercial polysaccharides. Water-soluble derivatives of polysaccharides can exhibit properties of biodegradable polymeric surfactants after appropriate chemical modification [1,2].

Starch is renewable, biodegradable, low-cost biopolymer and therefore represents an ideal raw material for production of biosurfactants. The recently reported hydrophobic modification methods used on starch are mainly based on physical treatments [3] and esterification reactions [4].

Partially hydrophobized CMS derivatives represent important biodegradable biosurfactants [5, 6]. An interesting alternative of the conventional hydrophobization methods, based on the esterification of carbohydrates with acid halides, anhydrides or by transesterification, represents the amidation of CMS with alkyl amines. Recently, a performing method of amidation of carboxymethylcellulose [7] and dextran [8] has been reported.

CMS is the most important ionic starch ether commercially produced in large quantities. The degree of substitution of the carboxymethyl groups of the commercial products was ranges from 0.1 to 0.4 and products are partially soluble in water.

2. EXPERIMENTAL

2.1 Materials and analytical methods

O-(carboxymethyl) starch with DS=0.3 and DS=0.1, methanol, dimethylsulfoxide(DMSO), dodecylamine was from FLUKA AG. RUCHS SG, Switzerland, hexylamine and decylamine was

purchased from SIGMA – Aldrich Chemie, Steinheim, Germany, 4 – Dimethylaminopyridine (DMAP) was from Merck, Darmstadt, Germany.

The derivatives were characterized by FT-IR spectral data (in KBr pellets, 2mg/200mg) obtained on the NICOLET Magna 750 spectrophotometer with a DTGS detector and OMNIC 3.2 software using 128 scans at a resolution of 4 cm⁻¹.

2.2 Amidation of Carboxymethylstarch (CMS)

1.0 g of CMS (in the H⁺ form) introduced into 15ml methanol (or DMSO) was stirred and 0.005g of dimethylaminopyridine as a catalyst was added. After that 5g or 2.5 g of dodecylamine (hexylamine, decylamine) in 15 ml methanol was added. The reaction mixture was stirred at room temperature for 21-31 h. or at temperature 45 - 50°C for 5-10 h. After that the product was filtered, washed with chloroform, and then dried. Obtained CMS alkylamides was dissolve in water and their pH values was established to 6.5 by pH meter using addition of 0.1 M HCl solution. CMS alkylamides were isolated from solution by lyofiltration.

2.3 Testing methods

The surface tension of aqueous solutions of the derivatives in the concentration range 0.155 – 0.625 g.l⁻¹ was measured at 25 °C using the Du Nouy ring apparatus. The surface tension (γ_{min}) and critical micelle concentration were determined graphically as described in a previous paper [9].

The stability of the emulsion was estimated at three different time intervals after the emulsions had been prepared, i.e. 5 min (h₁), 1 h (h₂) and 24 h (h₃), and expressed in terms of the height (mm) of oil and cream layers formed on the surface of the emulsion.

The washing power (WP) and antiredeposition efficiency (ARE) of the prepared derivatives at concentration 0.5 kg.m⁻³ was determined by the method described more detailed in a previous paper [5] using cotton fabric (SK-standard 800 101).

3. RESULTS AND DISCUSSION

3.1 Preparation and characterization CMS alkylamides

The amidation of CMS with alkylamine was carried out in methanol on the presence of DMAP as catalyst. Prepared CMS derivates at various reaction conditions are summarized in Table 1, 2.

Tab.1: Results of amidation of CMS (DS=0.3 or 0.1) with dodecylamine at various reaction conditions

	Sample	DS CMS	Mass ratio CMS:DDA	Time [h]	Yield (g/g)
I	SR-400AMID 10	0.1	1 : 5	21	0.95
II	SR-400AMID 11	0.1	1 : 5	31	0.91
III	SR-400AMID 12	0.1	1 : 10	21	0.86
IV	SR-400AMID 13	0.1	1 : 10	31	0.94
V	SR-400AMID 6	0.3	1 : 5	21	0.93
VI	SR-400AMID 6/2	0.3	1 : 5	10	0.96
VII	SR-400AMID 15	0.3 ^a	1 : 5	5	0.97
VIII	SR-400AMID 16	0.3 ^a	1 : 5	5	0.92
X	SR-400AMID 18	0.3	1 : 3	21	0.78

^a T = 45-50 °C and DMSO

Tab.2: Results of amidation of CMS (DS=0.3) with decyl – and hexylamine at various reaction conditions

	Sample	Temperature [C°]	Mass ratio CMŠ:DDA	Time [h]	Yield (g/g)
IX ^a	SR-400AMID 17	20	1 : 5	21	0.98
XI ^b	SR-400AMID 19	20	1 : 5	21	0.95
XII ^b	SR-400AMID 20	20	1 : 10	21	0.92

^a hexylamine ^b decylamine

As shown in FTIR spectra (Fig.1), the $\nu(\text{CONH})$ band, indicated by a weak shouder at 1606cm^{-1} , is overlaped by $\nu(\text{COO}^-)$ band. Therefore, Fourier self deconvolution method was used in order to confirm the presence of amid group (Fig.2). All prepared CMS derivates gave $\nu(\text{CONH})$ bands at 1559 and 1641 cm^{-1} , which was in agreement with literature[10].

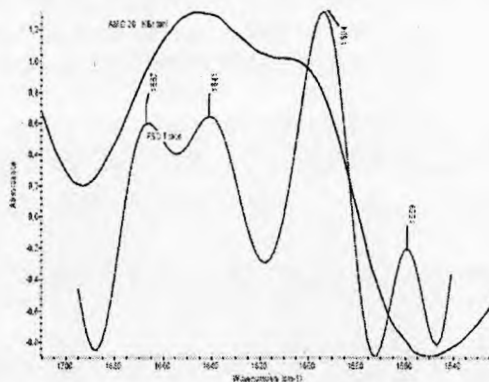
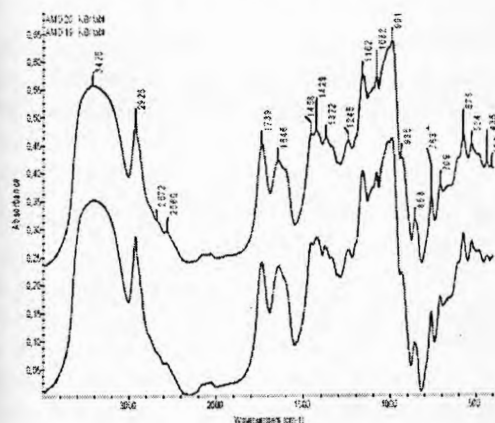


Fig.1: FT-IR spectra of CMS amides (XI, XII)

Fig.2: Decomposition of FT-IR spectrum (XII)

The surface – active properties of the prepared water –soluble CMS derivates were characterized by measuring of surface tension (γ_{\min}), the critical micelle concentration (c.m.c), washing power (WP), antiredeposition efficiency (ARE) and emulsifying efficiency (h_1 , h_2 , h_3). From the data in Table 3, it can be seen that derivates lowered the surface tension of water to 53.3 and 57.8 mN.m^{-1} . The c.m.c. ranged from 0.16 to 1.33 kg.m^{-3} .

Tab.3: Surface tension (γ_{\min}), critical micelle concentration (c.m.c) of modification derivates CMS

	DERIVATES	Reactants	γ_{\min} [mN.m ⁻¹]	c.m.c [kg.m ⁻³]
V	SR-400AMID 6	dodecylamine	53.3	0.29
VI	SR-400AMID 6/2	dodecylamine	57.8	0.16
VII	SR-400AMID15	dodecylamine	63.0	have not
IX	SR-400AMID 17	hexylamine	65.1	1.33
XI	SR-400AMID 19	decylamine	59.2	1.30
XII	SR-400AMID 20	decylamine	68.3	have not

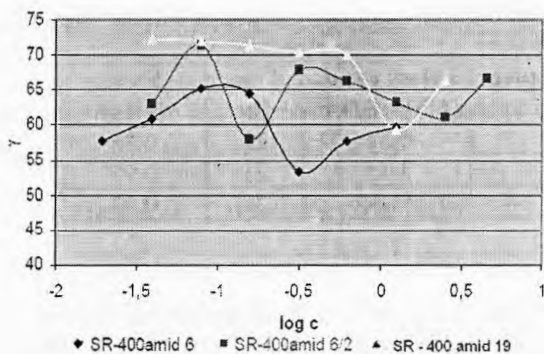


Fig. 3: Surface tension of derivatives V, VI, XI

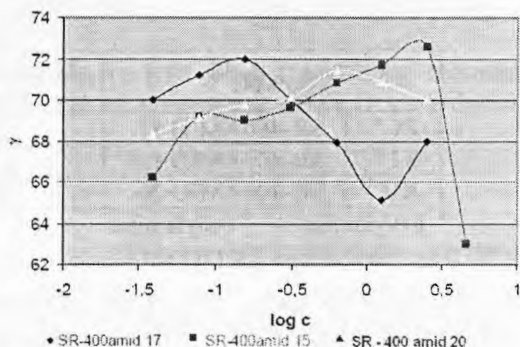


Fig.4: Surface tension of derivatives IX, VII, XII

Emulsifying efficiency was characterized by the stability of the parafinic oil/water emulsion of the derivatives CMS. The results, summarized in Table 4, show that derivatives CMS gave stable emulsions of the oil/water type and their efficiency is comparable to that of the commercial emulsifier Tween 20. In the case of samples IV, V and VI, a discretely separated oil layer appeared after 24 h. The starting CMS gave unstable emulsions.

Tab.4: Emulsifying efficiency after 5min (h_1), 1h (h_2) and 24 h (h_3), washing power (WP) and antiredeposition efficiency (ARE) some of the CMS amides

DERIVATES		h1 [mm]	h2 [mm]	h3 [mm]	WP [%]	ARE[%]
I ^a	SR-400AMID 10 - La	0/0	0,5/10	0,8/10	-	-
II ^a	SR-400AMID 11 - La	0/0	0/0	0/8	-	-
III ^a	SR-400AMID 12	0/0	0/6	0/10	-	-
IV ^a	SR-400AMID 13	0/0	0/0	0/0	-	-
V ^a	SR-400AMID 6- La	0/0	0/0	0/4	-	-
VI ^a	SR -400AMID 6/2- La	0/0	0/0	0/10	79	53.8
VII ^a	SR-400AMID 15 - La	1/5	4/1	5/0	-	-
IX ^b	SR-400AMID 17 - He	0/0	0/55	0/34	47	50.0
XI ^c	SR-400AMID 19- De	-	-	-	-	-
XII ^c	SR-400AMID 20 - De	4/14	5/14	5/14	69	43.0
	Tween 20	0/0	0/0	0/11	-	-
	CMŠ (DS=0.3)	-	-	-	38	23.9
	CMC (DS=1.0)	-	-	-	-	70.0
	Sodium dodecyl sulfate	-	-	-	53	-

^a - dodecylamine ^b - hexylamine ^c - decylamine - not determined

The washing power was carried out in a similar way to the method described in literature [5] at concentration $c_1=0.5 \text{ kg} \cdot \text{m}^{-3}$. Some of the derivatives were tested for their detergent performance by washing power (WP) and antiredeposition efficiency (ARE) using SDS as standards. The results shown in Tab.4 indicate that WP some of CMS amides was excellent and comparable to the standard SDS or higher. The antiredeposition efficiency was assessed for some derivatives CMS and was higher as starting CMS, but lower as standard CMC. The values of antiredeposition efficiency ranged from 43.0% to 53.8% (Table 4).

4. CONCLUSION

Alkylamidation of CMS leads to derivatives with enhanced – active and functional properties. Partial hydrophobization of CMS with various alkylamides such as lauryl, decyl and hexyl amine was performed in methanol and dimethylaminopyridine as catalyst. The new synthesized amides of CMS exhibited excellent stability oil/water type of emulsion with comparable to that of the commercial standard Tween 20. Washing power was excellent, too and compared to the sodium dodecylsulphate as control. Antireporedeposition activity was higher as starting CMS. The results suggested that the partially hydrophobized CMS derivatives are potential biosurfactants, which might be exploited in various technical applications.

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5. REFERENCES

- [1] Hodul, P., Antoš, K., Blažej, A., Markušovská, E.: *Tenside detergents* 22(1985)114-116.
- [2] Talába, P., Sroková, I., Hodul, P., Čík, G.: *Chem. Papers* 50 (1996) 101-104.
- [3] Fringant, C., Rinaudo, M., Forau, M.F. and Bardet, M.: *Carbohydr. Polym.* 35(1998)97-106.
- [4] Whistler, R.L., Madson, M.A., Zhao, J. And Daniel, J.R.: *Cereal Chem.* 75(1998)72-74.
- [5] Sroková, I., Miníková, S., Ebringerová, A., Sasinková, V., Heinze, TH.: *Tenside Surf. Det.* 40, 2003, 73.
- [6] Burczyk, B., *Encyclopedia of Surface and Colloid Science*, Marcel Dekker, ISBN: 0-8247-0859-8(2002)724.
- [7] Charpentier, D., Mocanu, G., Carpov, A., Chapelle, S., Merle, L., Miller, G., *Carbohydr. Polymers* 33(1997) 177-186.
- [8] RONEY, M.L.: *Polymer* 17, 1976, 555 - 558.
- [9] Sroková, I., Ebringerová, A., Heinze, TH.: *Tenside Surf. Det* 38, (2001), 277.
- [10] Milata, V., Segľa, P.: *Spektrálne metódy v chémii*, (2002), STU Bratislava.